



## Short communication

# Recycling of spent ion-lithium batteries as cobalt hydroxide, and cobalt oxide films formed under a conductive glass substrate, and their electrochemical properties

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## H I G H L I G H T S

- Cobalt recycling as  $\text{Co}(\text{OH})_2$  and  $\text{Co}_3\text{O}_4$  films formed under a conductive glass.
- Morphological and structural characterization of recycled  $\text{Co}(\text{OH})_2$  and  $\text{Co}_3\text{O}_4$  films.
- Electrochemical properties of  $\text{Co}(\text{OH})_2$  and  $\text{Co}_3\text{O}_4$  films under a conductive glass.

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## A B S T R A C T

In this work,  $\text{Co}(\text{OH})_2$  and  $\text{Co}_3\text{O}_4$  films have been obtained using a solution to leach the cathodes of spent Li-ion batteries. The  $\text{Co}(\text{OH})_2$  is electrodeposited onto conductive glass by the application of  $-0.85$  V, with a charge density of  $20 \text{ C cm}^{-2}$ , and its efficiency is found to be 66.67%. The  $\text{Co}_3\text{O}_4$  film is obtained by heat treatment of the  $\text{Co}(\text{OH})_2$  film at  $450^\circ\text{C}$  for 3 h, in an air atmosphere, with a conversion efficiency of 64.29%. The cyclic voltammetry of  $\text{Co}(\text{OH})_2$ , in  $\text{KOH } 1.0 \text{ mol L}^{-1}$  shows: three anodic peaks in the first cycle associated with the oxidation of  $\text{Co}(\text{OH})_2$  to  $\text{Co}_3\text{O}_4$ , the conversion of  $\text{Co}_3\text{O}_4$  into  $\text{CoOOH}$ , and the formation of  $\text{CoOOH}$  to  $\text{CoO}_2$  and the oxidation of water. The absence of cathodic peaks shows that oxidation from  $\text{Co}(\text{OH})_2$  to  $\text{CoO}_2$  is an irreversible process. For the  $\text{Co}_3\text{O}_4$  electrode, this verifies the existence of a redox pair associated with reversible oxidation of the  $\text{Co}_3\text{O}_4$  to  $\text{CoO}_2$ . The  $\text{Co}_3\text{O}_4$  obtains a charge efficiency of 77% for the first 10 cycles ( $1.0 \text{ mV s}^{-1}$ ) and a specific capacitance of  $31.2 \text{ F g}^{-1}$  ( $1.0 \text{ mV s}^{-1}$ ) and  $10.5 \text{ F g}^{-1}$  ( $10 \text{ mV s}^{-1}$ ).  $\text{Co}_3\text{O}_4$  films have promising applications as pseudocapacitors.

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## 1. Introduction

Worldwide economic expansion has brought about the phenomenon known as globalization, which has been facilitated by technological advances. As a result, there is a growing use of electronic devices that are dependent upon energy accumulators, especially portable devices, such as mobile devices, notebooks, smartphones, implantable medical devices, hybrid electric vehicles, etc. [1].

Today, Li-ion batteries is one of the primary models used in electronic devices because they have high energy density, low self-discharge rate, long life cycle, high electrical potential difference,

and low environmental impact [2]. The cathode of a Li-ion battery consists of a  $\text{LiCoO}_2$  layer over an aluminum current collector. The anode consists of carbon materials over a copper current collector, and the electrolyte contains inorganic Li salt dissolved in organic solvents [3,4].

Because of the increasing demand for electronic devices, environmental and economic concerns have surfaced. One example of these concerns is the discarding of the devices when they are depleted and the shortage of raw materials used to make the devices. With that being said, the technological advances in the search for more economical, efficient, and environmentally compatible materials, as well as the development of techniques for recycling these devices, is extremely relevant to society.

The recovery of cobalt, in the form of  $\text{Co}(\text{OH})_2$  and  $\text{Co}_3\text{O}_4$ , from the cathodes of Li-ion batteries is an interesting proposal because, according to the London Metal Exchange (LME) in March 2014, the price of cobalt was US\$ 30.2  $\text{kg}^{-1}$  [5]. Consequently,  $\text{Co}(\text{OH})_2$  and

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Co<sub>3</sub>O<sub>4</sub> films have received increasing attention from researchers because they have features that are compatible with various technological applications, such as supercapacitors, electrodes for batteries, electrochromic devices, as well as functioning as an additive for electrodes of Ni(OH)<sub>2</sub>, and as a catalyst [6–18]. The Co(OH)<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub> films have been prepared via electrodeposition in solutions that contain nitrate ions for application as supercapacitors, electrochromic devices, as an additive for electrodes of Ni(OH)<sub>2</sub>, and as a catalyst. The alkalization of the electrode/solution interface occurs due to the reduction of both nitrate and water. Then, the precipitation of Co(OH)<sub>2</sub> occurs, as can be seen in the following equations [19–21]:



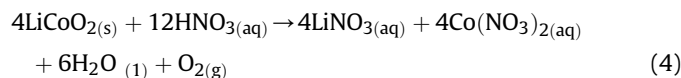
This work aims to associate the electrochemical recycling of the cobalt that is present in Li-ion depleted batteries with the properties of recycled Co(OH)<sub>2</sub> and the Co<sub>3</sub>O<sub>4</sub> films formed under glass substrate coated with indium-doped tin oxide (ITO) for possible applications in pseudocapacitors, electrochromic windows, and as catalysts. In this study, Co<sub>3</sub>O<sub>4</sub> was obtained by heat treatment of electrodeposited Co(OH)<sub>2</sub> on ITO. The Co<sub>3</sub>O<sub>4</sub> films obtained from the heat treatment of Co(OH)<sub>2</sub> demonstrates good efficiency and reversibility in the voltammetric and galvanostatic charge and discharge cycles. The electrochemical behavior of the materials was evaluated by cyclic voltammetry and the charge and discharge cycles were observed. For characterization, X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques were applied.

## 2. Experimental procedure

### 2.1. Preparation of the electrodeposition bath

Spent Samsung Li-ion batteries were dismantled manually and separated into their basic components: cathode, anode current collector, and involucre. The cathode was dried at 120 °C for 24 h. After drying, the cathode was placed in distilled water at 40 °C for one hour. During this period, separation of the active material (LiCoO<sub>2</sub>) from the current collector (Al) occurs. After separation from the current collector and washing, the active material was dried at 60 °C for 24 h.

For preparation of the electrodeposition bath, 10.0 of the cathode material was dissolved in 1.0 L of HNO<sub>3</sub> 3.0 mol L<sup>−1</sup> solution with stirring for 2 h at 80 °C. The dissolution of the cathode solution was filtered, removing the insoluble materials, such as carbon black, that make up the electrode. The dissolution process is represented by the following chemical equation:

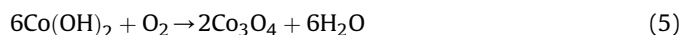


### 2.2. Preparation and characterization of the Co(OH)<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub> films

The pH of the dissolution of the cathode solution was 6.5 with the addition of KOH powder, and the solution was buffered with H<sub>3</sub>BO<sub>3</sub> 0.1 mol L<sup>−1</sup>. The working electrodes were made with glass coated with a film of indium-doped tin oxide (ITO), with an active area of 0.5 cm<sup>2</sup>. The ITO substrates were washed with detergent and distilled water, and then they were placed in an ultrasound bath for

10 min. Afterwards, they were cleaned with ethanol, acetone, and isopropyl alcohol and finally dried in a room environment temperature. The counter electrode was graphite with 99% purity and an area of 3.0 cm<sup>2</sup>.

The parameters for the electrodeposition of the Co(OH)<sub>2</sub> films under ITO were determined through cyclic voltammetry (CV), with a scan rate of 10.0 mV s<sup>−1</sup>, beginning from 0.50 V and switching to the cathode potential of −1.10 V and then returning to 0.50 V vs Ag/AgCl. The electrodeposition of Co(OH)<sub>2</sub> on the ITO substrate was performed by applying the potential of −0.85 V vs Ag/AgCl and the charge density of 20.0 C cm<sup>−2</sup>. A mass of 0.0032 g (66.67% relative to theoretical mass of 0.0048 g), of the Co(OH)<sub>2</sub> precursor material was obtained by potentiostatic electrodeposition on ITO. The mass efficiency was of 66.67% because the electrodeposition of Co(OH)<sub>2</sub> onto the ITO substrate occurs after alkalization of the electrode/solution interface through nitrate reduction. After alkalization of the electrode solution interface and the solubility of the product is achieved, the Co(OH)<sub>2</sub> film precipitates onto the ITO. The Co(OH)<sub>2</sub> film is nonconductive and blocks the passage of current. Therefore, only part of the charge is used to reduce the nitrate ion and subsequent precipitation of Co(OH)<sub>2</sub>. After the Co(OH)<sub>2</sub> films were formed on ITO by electrodeposition, the electrodes (Co(OH)<sub>2</sub> films and ITO substrate) were washed and calcined at 450 °C for 3 h to obtain Co<sub>3</sub>O<sub>4</sub> [22]. The chemical transformation that the calcinated material underwent can be represented by the chemical Equation (5): [19]



The efficiency of conversion of Co(OH)<sub>2</sub> to Co<sub>3</sub>O<sub>4</sub> is 64.29% w/w due to the loss of material during washing and calcination. The mass loss could be caused by lack of adhesion between the Co(OH)<sub>2</sub> film and ITO substrate.

The electrochemical properties of Co(OH)<sub>2</sub> occurred in the range of −0.4 V to 0.6 V, and returned to −0.4 V to 0.5 V. The electrochemical properties of the Co<sub>3</sub>O<sub>4</sub> electrodes were analyzed using cyclic voltammetry (CV); the initial potential of those electrodes ranged from 0.4 V to the vertex potential of 0.6 V, and then the potential was returned to 0.4 V, with rate scans of 1.0 mV s<sup>−1</sup> and 10 mV s<sup>−1</sup>. The reference electrode and the counter electrode were Hg/HgO and the graphite (area 3.0 cm<sup>2</sup>), respectively. The electrolyte solution used was KOH 1.0 mol L<sup>−1</sup> without stirring at 25 °C. The galvanostatic charge and discharge cycles are made with current of 111.1 mA g<sup>−1</sup>, the charge and discharge time of 60 s, and the active material mass of 0.0018 g.

All the electrochemical measurements were performed using Autolab PGSTAT 302N potentiostat/galvanostat equipment with an electrochemical impedance spectroscopy module (EIS), coupled without stirring at 25 °C.

The X-ray diffraction measurements were performed using a BRUKER model D2 PHASER® with Cu Ka radiation (λ = 1.5406 Å) and a scan rate of 2 min<sup>−1</sup>. Scanning Electron Microscopy (SEM) of the Co(OH)<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub> were performed using a scanning electron microscope, JEOL 6610LV.

## 3. Results and discussion

### 3.1. Electrochemical formation and characterization of the Co(OH)<sub>2</sub> film growth on the ITO substrate

The cyclic voltammogram for the electrodeposition of the Co(OH)<sub>2</sub> films on the ITO substrate at a scan rate of 10 mV s<sup>−1</sup> is represented in Fig. 1. The formation of Co(OH)<sub>2</sub> on the surface of the electrodes occurs in the electrochemical and chemical steps. In a direct scan there is an increase in the current density from −0.6 V

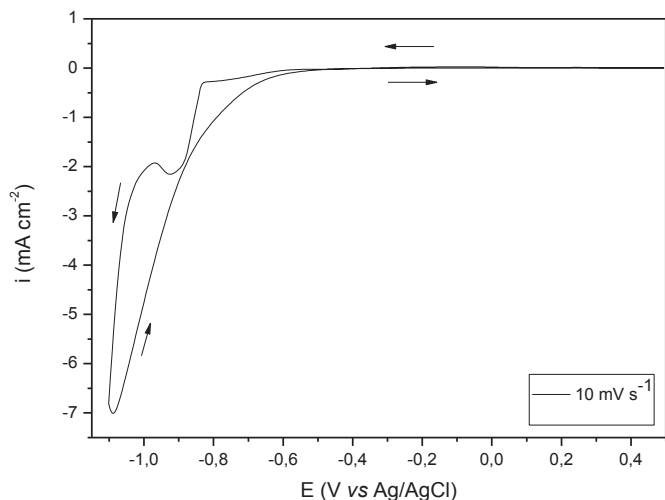


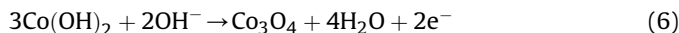
Fig. 1. Typical cyclic voltammogram for cobalt hydroxide electrodeposition on ITO substrate, at scan rate of  $1.0 \text{ mV s}^{-1}$ .

and a peak at  $-0.9$  due to the reduction of the nitrate ions and the water that contains dissolved oxygen. The alkalinizing of the electrode/solution interface and the formation of  $\text{Co}(\text{OH})_2$  on ITO occurs, as described in Equations (1)–(3). From a potential ranging from  $-0.9$  V to  $-1.1$  V, and in the reverse scanning in which the potentials range from  $-1.1$  V to  $-0.6$  V, the reduction reactions of the nitrate ions, of the water, and the precipitation of  $\text{Co}(\text{OH})_2$  occur simultaneously.

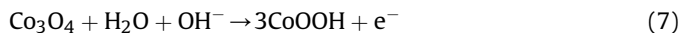
The  $\text{Co}(\text{OH})_2$  films were prepared by applying the potential of  $-0.85$  V vs Ag/AgCl and the charge density of  $20.0 \text{ C cm}^{-2}$ . The cyclic voltammetry technique was applied to evaluate the behavior of the  $\text{Co}(\text{OH})_2$  film in a  $1.0 \text{ mol L}^{-1}$  KOH solution. Fig. 2 shows the cyclic voltammograms obtained for the  $\text{Co}(\text{OH})_2$  electrode on the 1st and 10th cycles at  $10 \text{ mV s}^{-1}$ . In the 1st cycle, three anodic peaks are observed at  $0.19$  V,  $0.30$  V, and  $0.35$  V, but no cathodic peaks are observed. The peak at  $0.19$  V is associated with the oxidation of  $\text{Co}(\text{OH})_2$  to  $\text{Co}_3\text{O}_4$ . In the peak at  $0.30$  V, the  $\text{Co}_3\text{O}_4$  becomes  $\text{CoOOH}$ ; at  $0.35$  V,  $\text{CoOOH}$  converts to  $\text{CoO}_2$  and the water undergoes oxidation. These results indicate that the  $\text{Co}(\text{OH})_2/\text{ITO}$  electrode is an interesting catalyst to promote water oxidation. The absence of cathodic peaks suggests that the oxidation of  $\text{Co}(\text{OH})_2$  to  $\text{CoO}_2$  is an

irreversible process. The chemical Equations (6)–(9) describe that process [23–26], as follows:

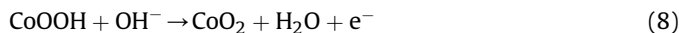
The peak at  $0.19$  V:



The peak at  $0.30$  V:



The peak at  $0.35$  V:



### 3.2. Electrochemical properties of the $\text{Co}_3\text{O}_4$ films

Fig. 3 shows the cyclic voltammograms for the  $\text{Co}_3\text{O}_4$  films. As can be seen, there are anodic and cathode peaks at  $0.54$  V and  $0.49$  V, respectively, for the scan rate of  $1.0 \text{ mV s}^{-1}$ . For the scan rate of  $10 \text{ mV s}^{-1}$ , there are anodic and cathode peaks at  $0.56$  V and  $0.46$  V, respectively, indicating that the active material  $\text{Co}_3\text{O}_4$  undergoes a reversible transformation to  $\text{CoOOH}$ , according to Equation (10) [27,28]:

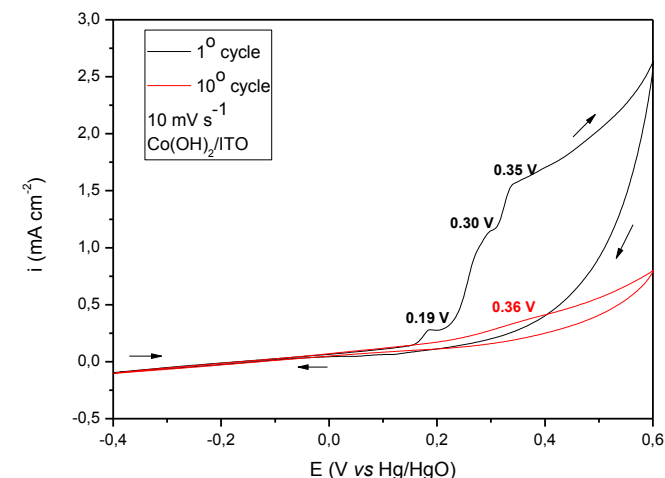
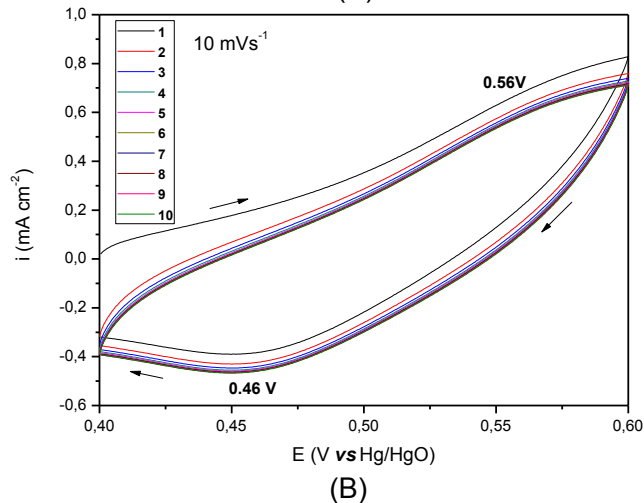
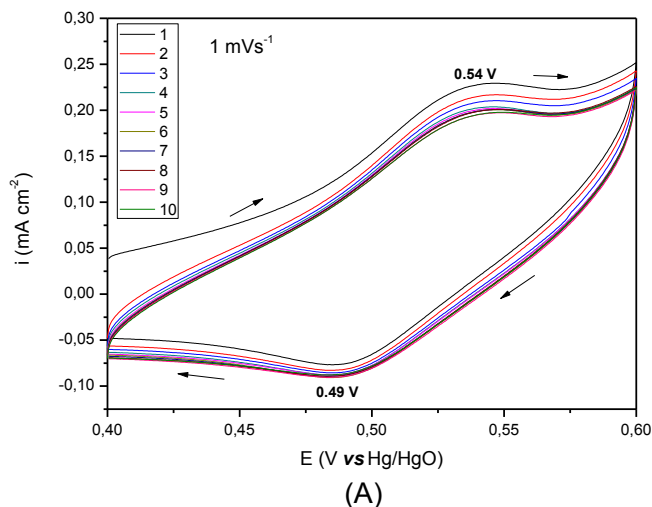


Fig. 2. Typical cyclic voltammograms performed for  $\text{Co}(\text{OH})_2$  film on ITO at  $10 \text{ mV s}^{-1}$  in KOH  $1.0 \text{ mol L}^{-1}$ .

Fig. 3. Typical cyclic voltammograms performed for  $\text{Co}_3\text{O}_4$  on ITO, A) at  $1.0 \text{ mV s}^{-1}$  and B) at  $10 \text{ mV s}^{-1}$  in KOH  $1.0 \text{ mol L}^{-1}$ .

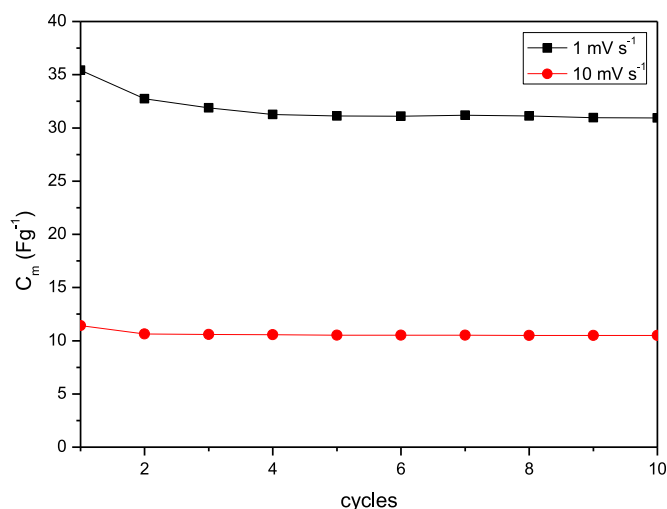
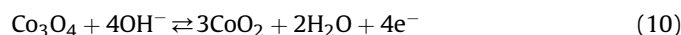


Fig. 4. Specific capacitance for  $\text{Co}_3\text{O}_4$  film on ITO (at 1.0 and 10  $\text{mV s}^{-1}$ ).



One can verify that, for the  $\text{Co}_3\text{O}_4$  electrode, the peaks due to the reaction represented by Equation (10) are displaced for more positive potential because of an increase in the resistance of the ITO electrode after the heat treatment at  $450^\circ\text{C}$  for 3 h. The resistance after the heat treatment was equal to  $148.3\ \Omega$ .

The reversible process of the  $\text{Co}_3\text{O}_4$  films is an important electrochemical behavior that has implications for their future application as supercapacitors and electrochromic materials.

The values of the densities of the anodic and cathodic charges found in each cycle can be used to evaluate the efficiency of the charge–discharge process. The charge efficiency ( $\alpha$ ) is given by:

$$\alpha = q_{\text{discharge}} / q_{\text{charge}} \quad (11)$$

The charge efficiency of 77% was obtained after 10 cycles of  $\text{Co}_3\text{O}_4$  electrodes at the scan rate of  $1.0\ \text{mV s}^{-1}$ .

The specific capacitance ( $C_m$ ) of the  $\text{Co}_3\text{O}_4$  electrodes is given by the following equation:

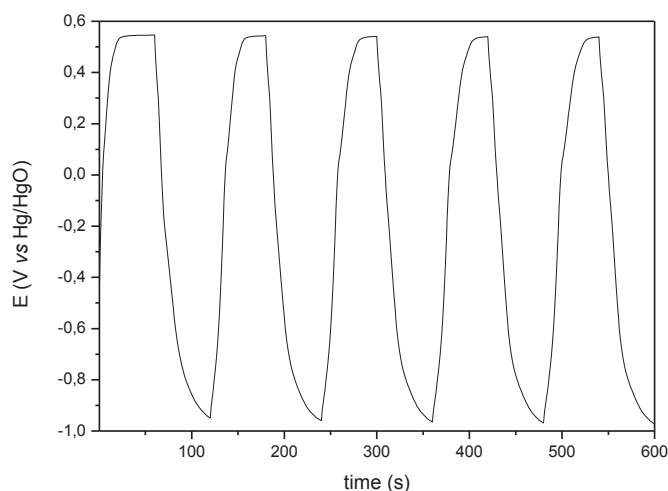


Fig. 5. Charge and discharge cycles for  $\text{Co}_3\text{O}_4$  on ITO in  $\text{KOH}\ 1.0\ \text{mol L}^{-1}$ , current of  $111.1\ \text{mA g}^{-1}$ , charge and discharge time of 60 s, and the active material mass of  $0.0018\ \text{g}$ .

$$C_m = Q / m\Delta V \quad (12)$$

where  $Q$  is the cathodic charge obtained with the GPES software,  $m$  is the mass of  $\text{Co}_3\text{O}_4$ , and  $\Delta V$  is the variation of the final and initial potential scan.

For the  $\text{Co}_3\text{O}_4$  films, the specific capacitance over 10 cycles, ranging from  $1.0\ \text{mV s}^{-1}$  and  $10\ \text{mV s}^{-1}$ , are shown in Fig. 4. The specific capacitance for  $1.0\ \text{mV s}^{-1}$  and  $10\ \text{mV s}^{-1}$  were about  $31.2\ \text{F g}^{-1}$ , and  $10.5\ \text{F g}^{-1}$ , respectively. It is observed that the scan specific capacitance is higher for the lower scan rate; this occurs because the diffusion of the electroactive electrolyte to the electrode surface is more effective and, consequently, the reactions of the charge transfers are favored.

The charge and discharge cycles are represented in Fig. 5, and they show good repeatability of the process undergone, which confirms that this oxide is a promising candidate for use in making electrode material. The charge and discharge current are  $111.1\ \text{mA g}^{-1}$ , and the specific capacitance of  $4440\ \text{mF g}^{-1}$ .

### 3.3. Characterization of the $\text{Co}(\text{OH})_2$ and $\text{Co}_3\text{O}_4$ films by XRD and SEM

The  $\text{Co}(\text{OH})_2$  obtained by electrochemical precipitation on the ITO electrode presented an hexagonal crystal structure (JCPDS 30–443); the peaks of this structure are shown in Fig. 6A.

The typical XRD pattern for the  $\text{Co}_3\text{O}_4$  obtained on the ITO electrode is shown in Fig. 6B. The peaks are related to  $\text{Co}_3\text{O}_4$  with a

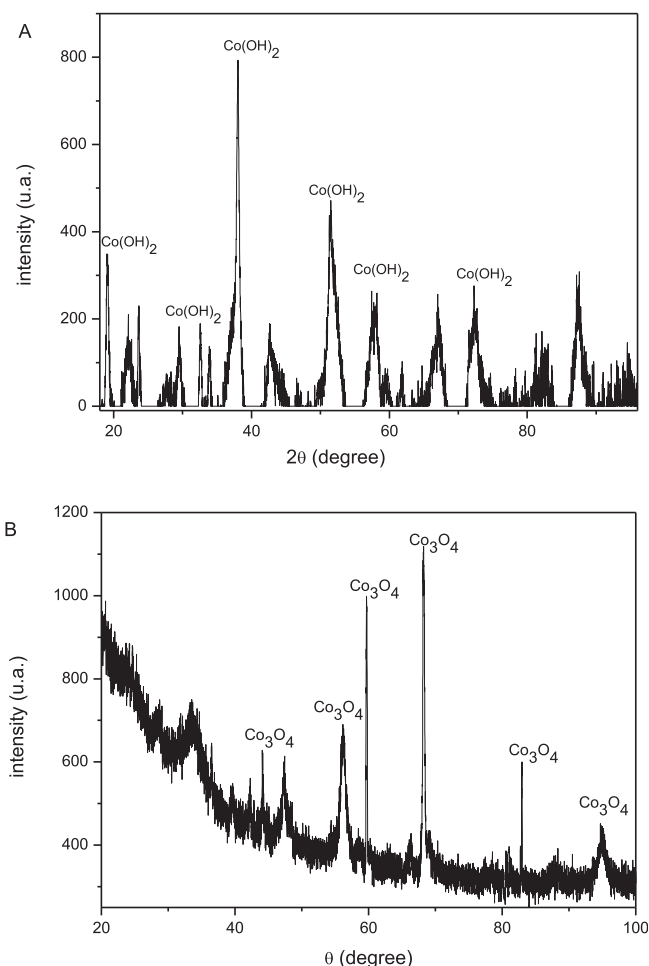
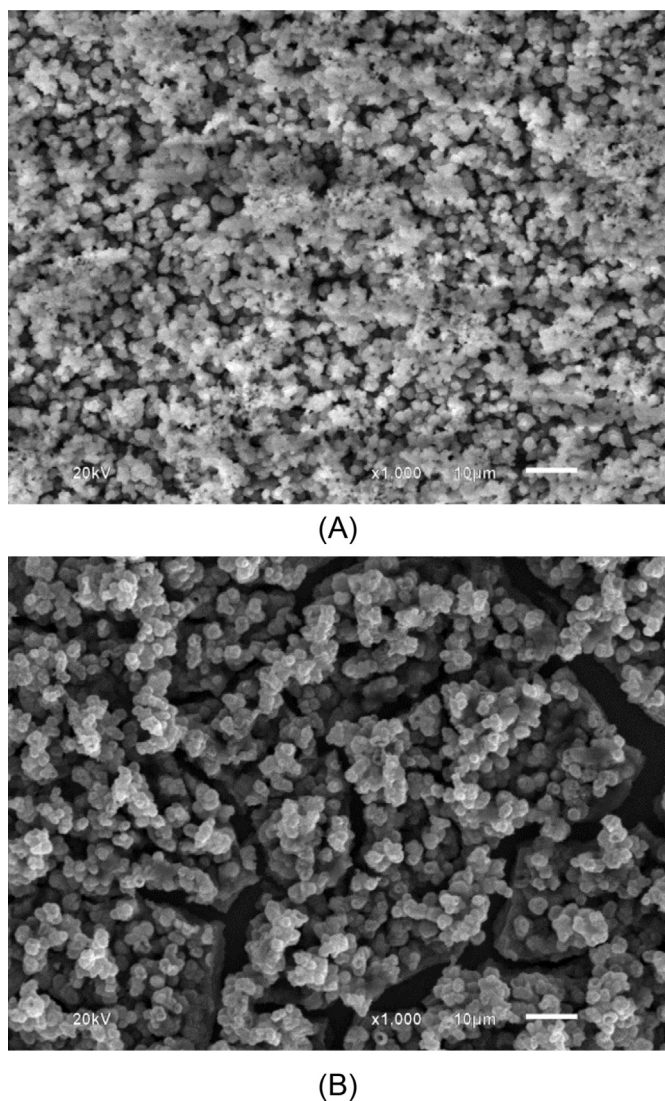


Fig. 6. X-ray diffraction spectrum, A)  $\text{Co}(\text{OH})_2$  recovered by electrochemical precipitation ( $20\ \text{C cm}^{-2}$ ) and B)  $\text{Co}_3\text{O}_4$  synthesized via  $\text{Co}(\text{OH})_2$  calcination.





**Fig. 7.** Micrographs, A)  $\text{Co(OH)}_2$  electrodeposited on ITO ( $20 \text{ C cm}^{-2}$ ) and B)  $\text{Co}_3\text{O}_4$  synthesized via  $\text{Co(OH)}_2$  calcination.

cubic structure (JCPDS 43–1003). Fig. 7 shows the micrographs of the  $\text{Co(OH)}_2$  and  $\text{Co}_3\text{O}_4$  films. In Fig. 7A, the micrograph of the electrodeposited  $\text{Co(OH)}_2$  reveals a very porous morphology with particles smaller than  $10 \mu\text{m}$  that cover the entire substrate. As shown in Fig. 7B, after the heat treatment, fissures have appeared due to the desorption of the water and the impurities and the dehydroxylation reaction of  $\text{Co(OH)}_2$  with the formation of  $\text{Co}_3\text{O}_4$ . That figure also shows an increase in the particle size as well as the formation of clusters of  $\text{Co}_3\text{O}_4$  where the diffusion of the electrolyte on the electrode surface and the reactions of the charge transfers occur. These structures significantly support the redox activity, which reinforces the application of these materials in electrochemical devices.

#### 4. Conclusions

In this work,  $\text{Co(OH)}_2$  and  $\text{Co}_3\text{O}_4$  were obtained using a solution to leach the cathodes of spent Li-ion batteries. The  $\text{Co(OH)}_2$ , the source material to the  $\text{Co}_3\text{O}_4$  synthesis, was electrodeposited onto the ITO substrate by the application of  $-0.85 \text{ V}$  vs  $\text{Ag/AgCl}$ , with the charge density of  $20 \text{ C cm}^{-2}$ , and its efficiency was 66.67%. By the

heat treatment of  $\text{Co(OH)}_2/\text{ITO}$  for 3 h at  $450^\circ\text{C}$ , in an air atmosphere,  $\text{Co}_3\text{O}_4/\text{ITO}$  was obtained and it showed a conversion efficiency of 64.29%. XRD verified that the electrodeposit of  $\text{Co(OH)}_2$  exhibited a hexagonal structure, while the obtained  $\text{Co}_3\text{O}_4$  showed a cubic structure. The scanning electron microscopy (SEM) showed that the electrodeposition of  $\text{Co(OH)}_2$  was recovered on the ITO substrate, and it has a very porous surface with grains smaller than  $10 \mu\text{m}$ . Using the heat treatment of  $\text{Co(OH)}_2$  to obtain  $\text{Co}_3\text{O}_4$  resulted in the appearance of fissures, due to the impurities and water's desorption and the dehydroxylation of  $\text{Co(OH)}_2$ . An increase of the particle size and the formation of  $\text{Co}_3\text{O}_4$  clusters were also noticed, which makes the diffusion of the electrolyte and charge transfer reactions easier, and that supports the application of these materials in electrochemical devices.

In cyclic voltammetry of  $\text{Co(OH)}_2/\text{ITO}$  (1st cycle) three anodic peaks (vs  $\text{Hg/HgO}$ ) were observed, indicating that at  $0.19 \text{ V}$  the oxidation of the  $\text{Co(OH)}_2$  to  $\text{Co}_3\text{O}_4$  occurs, at  $0.30 \text{ V}$  the  $\text{Co}_3\text{O}_4$  is converted into  $\text{CoOOH}$ , and at  $0.35 \text{ V}$  the  $\text{CoOOH}$  is transformed into  $\text{CoO}_2$  and water oxidation occurs. This indicates that the  $\text{Co(OH)}_2/\text{ITO}$  electrode is an interesting catalyst for the oxidation of water. The absence of cathodic peaks shows that oxidation from  $\text{Co(OH)}_2$  to  $\text{CoO}_2$  is an irreversible process. For the  $\text{Co}_3\text{O}_4/\text{ITO}$  electrode, this finding verifies the existence of a redox pair, at  $0.54 \text{ V}/0.49 \text{ V}$  ( $1.0 \text{ mV s}^{-1}$ ) and  $0.56 \text{ V}/0.46 \text{ V}$  ( $10 \text{ mV s}^{-1}$ ), associated with the reversible oxidation of  $\text{Co}_3\text{O}_4$  to  $\text{CoO}_2$ . This electrode demonstrated a charge efficiency of 77% for the first 10 cycles ( $10 \text{ mV s}^{-1}$ ), specific capacitance of  $31.2 \text{ F g}^{-1}$  ( $1.0 \text{ mV s}^{-1}$ ) and  $10.5 \text{ F g}^{-1}$  ( $10 \text{ mV s}^{-1}$ ), and charge/discharge's cycles with good repeatability. Therefore, these electrochemical behaviors suggest that the  $\text{Co}_3\text{O}_4$  electrode shows promising characteristics for applications in electrocatalysis and as pseudocapacitors.

In addition to providing important parameters for developing new technologies, this study demonstrates that obtaining  $\text{Co(OH)}_2$  and  $\text{Co}_3\text{O}_4$  from recycled Li-ion batteries is possible and this finding adds value to a product that could be eventually improperly discarded and potentially harmful to human health and the environment.

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